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Formaldehyde Release From Labeled and Unlabeled Cross-Linked Cotton and Cotton-Polyester Fabrics



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Formaldehyde Release From Labeled and Unlabeled Cross-Linked Cotton and Cotton-Polyester Fabrics

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ABSTRACT

The cross-linking agent used for treating the all-cotton and 50/50 cotton-polyester fabrics tested in this study was unisolated dimethyloldihydroxyethyleneurea (DMDHEU) prepared by either two- or three-component synthesis using labeled (^{14}C) formaldehyde. These labeled fabrics were prepared for future animal exposure tests. Tests were also conducted with unlabeled fabrics treated with a similarly synthesized cross-linking agent. Formaldehyde release from the fabrics was measured by using the cold sodium sulfite method or the sealed-jar method. The conditions evaluated included laundering fabrics with and without chlorine bleach and drying them under various conditions; exposing fabrics to a carbon arc after tumble-drying; laundering fabrics 5, 10, 15, or 25 times and tumble-drying; and storing samples for 1, 2, 3, or 12 months. Also, wrinkle recovery of the fabrics was determined. In general, there was little effect on formaldehyde release, whether the DMDHEU was prepared from two or three components. Formaldehyde release values generally declined with laundering and storage. But there were exceptions to the generally low values from the cold sodium sulfite method for samples after the spin-dry cycle (before drying), after exposure to the carbon arc, and after laundering five times. Index terms: cold sodium sulfite method, cotton fabrics, cotton-polyester fabrics, cross-linking agents, dimethyloldihydroxyethyleneurea (DMDHEU), formaldehyde release, sealed-jar method, wrinkle recovery angles.

INTRODUCTION

Studies on formaldehyde release have been performed by many research groups. Unfortunately, a number of different analytical methods have been employed, which frequently makes comparison of results difficult. Even when supposedly identical methods have been used by different research groups, results have sometimes varied.

The extensive work in formaldehyde release from textiles that has been performed by researchers at the Southern Regional Research Center (SRRC) in New Orleans, La., provides a common body of information from a single organization. Because SRRC carried out the textile treatments and evaluations in this study, a review of published work performed at the Center is relevant. These publications deal with the test methods used, the variables that influence formaldehyde release, the methods for controlling

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formaldehyde release, the theory of cross-linking, the hydrolysis of finishing agents, and the role of catalysts. A given paper may encompass several areas.

Formaldehyde release in sealed-jar experiments, which could be viewed as a forerunner of the present-day sealed-jar test of the American Association of Textile Chemists and Colorists (AATCC) (1978c) was reported by Reid et al. (1960). The methodology for free formaldehyde determination using a cold sodium sulfite method was reported by Moran and Vail (1965). In recent years, SRRC researchers, using various test methods, have become more concerned with what is measured by various formaldehyde tests (Vail and Andrews 1979, Andrews and Harper 1980, Vail and Reinhardt 1981), modifying such tests (Andrews, Reinhardt et al. 1980), and the influence of the finishing process or washing variables on formaldehyde release (Kullman et al. 1978, Reinhardt et al. 1981). In areas of controlling formaldehyde release, the use of additives and aftertreatments was first reported by Reid et al. (1962). A series of papers followed that gave detailed modifications for lowering formaldehyde release in cross-linking with carbamates (Frick and Reinhardt 1967, Reid et al. 1970, 1971). The use of steam treatments as a means of reducing free formaldehyde and formaldehyde release was also suggested (Reinhardt and Kullman 1971, Reinhardt et al. 1972). More recent work has focused on the use of lower levels of formaldehyde in the finish (Frick and Harper 1979) and on the role of structure, curing conditions, and catalyst concentrations on formaldehyde release (Andrews, Harper, and Vail 1980). Finally, additives such as polyols (Andrews, Harper, Smith et al. 1980) or hydrazides (Cashen 1979a, 1979b; Turner and Cashen 1981) have been demonstrated as a chemically effective approach for reducing formaldehyde release.

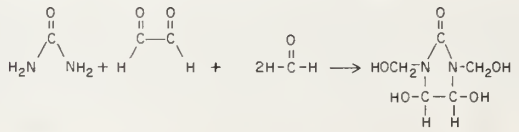
The theory of cross-linking and the resistance of finishes to hydrolysis have been the subject of numerous SRRC publications (Reeves et al. 1962; Andrews et al. 1962; Vail et al. 1969; Vail 1972, 1979; Vail and Pierce 1973; Pierce et al. 1976). These studies included both acid and base hydrolysis (Andrews et al. 1962, Vail and Pierce 1973). We know that formaldehyde release from a finish is directly related to its ease of hydrolysis. We also know that hydrolysis rate varies according to the structure of the cross-linking agent.

The research in this study was concerned primarily with formaldehyde-release and formaldehyde transport properties of cotton-containing fabrics that were treated with formaldehyde-based cross-linking agents. The work was performed at SRRC and the Richard B. Russell Agricultural Research Center (RRC) in Athens, Ga. Because its personnel have extensive experience and expertise in textile chemistry, SRRC was selected to perform that phase of the project concerned with the treatment and evaluation of fabric. Similarly, because of its expertise and facilities for work with laboratory animals, RRC was selected to perform the evaluation of the transport or transfer of released formaldehyde from a treated fabric to an animal.

Durable-press cotton and cotton-polyester fabrics were prepared at SRRC by treatment with a cross-linking agent containing carbon-14(^{14}C). The cross-linking agent was unisolated dimethyloldihydroxyethyleneurea (DMDHEU) prepared from either two or three chemical components. Patches of these labeled fabrics were to be applied to rabbits at RRC so that transfer of activity from fabric, through or into the rabbit skin and to selected organs, could be determined. The synthesis of the cross-linking agent (DMDHEU) was performed using ^{14}C-labeled formaldehyde so that any transfer of activity would be ascribable to the formaldehyde component.

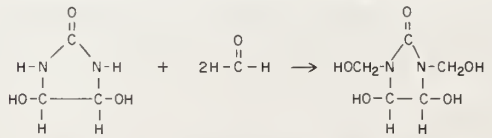
The DMDHEU was synthesized by the two procedures given below. DMDHEU is the most used cross-linking agent in the textile industry today. Its use became widespread in the 1960's with the advent of durable press. Its suitability as a delayed curing agent and its better stability to acid hydrolysis were factors in its becoming the dominant textile-finishing agent.

PROCEDURE A, commercial method (three-component synthesis):



UREA + GLYOXAL + FORMALDEHYDE → DMDHEU

PROCEDURE B, laboratory method (two-component synthesis):



DHEU + FORMALDEHYDE → DMDHEU

The DMDHEU solution was prepared in procedure A by the reaction of urea, glyoxal, and formaldehyde without isolation of the intermediate dihydroxyethyleneurea (DHEU). This technique corresponded to the usual route for the commercial preparation of DMDHEU. DMDHEU was prepared in procedure B from isolated DHEU, the cyclic product of urea and glyoxal, and formaldehyde. Because the intermediate (DHEU) was isolated (which made this a two-component synthesis), we thought that procedure B would yield a somewhat purer DMDHEU solution. In each synthesis, the formaldehyde component contained some ^{14}C-labeled formaldehyde so that the radioactivity in the final agent would be derived from formaldehyde.

In this study, personnel at SRRC performed chemical and textile tests on labeled fabrics and unlabeled fabrics from treatments with similarly synthesized cross-linking agents to determine the influence of the variables in laundering and storing of these fabrics on formaldehyde release. Certain ancillary experiments were also performed to broaden the scope of the project. This report covers the work performed at SRRC; the work performed at RRC will be covered in a separate report.

MATERIALS AND METHODS

Fabrics

Two fabrics of different fiber content were used for this study. One fabric was 100% cotton and the other an intimate blend of 50% cotton and 50% polyester. Both fabrics were sheetings weighing 4.1 oz/yd^2. Because both fabrics were prepared using yarns of the same size, the same thread count in warp and fill, and the same plain weave structure, the only difference between the two was in fiber content. The fabrics were desized, scoured, and bleached before finishing with cross-linking agent.

Chemicals

The urea was a reagent-grade chemical from Aldrich Chemical Co. Except for labeled formaldehyde, the formaldehyde used was from a commercial formalin solution containing 36.2% formaldehyde by analysis and 10%–15% methanol. The glyoxal used was a 40% solution obtained from a commercial source. The DHEU (m.p. 123°–136° C) was prepared from urea and glyoxal by modification of a procedure described earlier by Frick and Harper (1981). In this modification, pH was carefully controlled at 7.8–8.2 during a 3-day reaction period; then the solution was chilled and the precipitate collected. The product was recrystallized from water.

The ^{14}C-labeled formaldehyde (specific activity =20 millicuries per millimole (mCi/mmol) in 2.8%–4.5% aqueous solution) was obtained from Pathfinder Laboratories. The zinc nitrate catalyst was a reagent-grade chemical. Triton X-100 was used as a wetting agent.

Reagent Preparation and Application to Fabrics

DMDHEU was prepared by the two procedures given below. The reactions are shown graphically in the introduction to this report.

Procedure A, commercial process (three components).—A mixture (based on percentage of weight) of 12.55% water, 35.16% of 40% glyoxal, and 37.28% of 37% formaldehyde (formalin) was placed in a vessel suitable for refluxing and agitation of the mixture. Agitation was started, and the pH of the mixture was adjusted to 5.2–5.6 with 22% potassium hydroxide (KOH). Urea (14.63%) was added to the mixture, and the temperature was raised from 25° to 80° C and held there for a minimum of 2 hours. During the heating period, the pH was adjusted at 20-minute intervals to 5.5–5.9 with KOH, as required, with the first adjustment being made when the temperature reached 80° C. Additional heating at 80° C and pH adjustments were required for some preparations to reduce the free formaldehyde below 0.5%. The reaction vessel was cooled, and the pH of the solution was adjusted to 5.7–5.9.

Procedure B, laboratory process (two components).—A mixture (based on percentage of weight) of 23.05% water, 43.45% of 37% formaldehyde (formalin), and 33.50% isolated DHEU was placed in a reaction vessel equipped for refluxing and agitation of the mixture. The procedures for pH adjustments and heating of the mixture were the same as for the commercial-type procedure, with final pH adjustments being 5.9–6.15. The period of maintaining heat at 80° C was reduced from 2 hours to 75 minutes.

Radiolabeled DMDHEU.—Radiolabeled DMDHEU of the desired level of radioactivity was prepared with each of the above procedures by substituting the required amount of ^{14}C-labeled formaldehyde for an equivalent amount of unlabeled formaldehyde in the mixtures. A Packard model 3255 Tri Carb Liquid Scintillation Spectrometer system was used to establish the total radioactivity of each solution.

Treatment of all-cotton and 50/50 cotton-polyester sheetings with unlabeled or radiolabeled DMDHEU.—Aqueous padbaths containing 9% DMDHEU (unlabeled), 0.5% $ZN(NO_3)_2 \cdot 6H_2O$, and 0.1% Triton X-100 were prepared for treatment of the fabrics with unlabeled DMDHEU that was synthesized by both procedures. Fabric samples were padded through the solutions by the two-dip, two-nip method for an average wet pickup of 94.5% for the all-cotton sheeting and 78.5% for the 50/50 cotton-polyester sheeting. In this procedure, the fabric was immersed in a solution, squeezed between pressure rolls, reimmersed in the solution, and squeezed again. Wet pickup was based upon weight of solution picked up per weight of fabric being treated.

Aqueous solutions containing 8.0% DMDHEU (radiolabeled), 0.45% $Zn(NO_3)_2 \cdot 6H_2O$, and 0.1% Triton X-100 were prepared from ^{14}C-labeled DMDHEU for fabric treatments. Because of radiation safety requirements and the limited amount of solution prepared to maintain the needed level of radioactivity, the two-dip, two-nip method could not be used for padding or impregnating samples with treating solution. Instead, fabric samples (22 by 25 cm) were impregnated by rolling the pieces of fabric around a glass tube or rod (1.5 cm in diameter and 23 cm in length) and then inserting the tube and fabric into a stoppered test tube or cylinder containing the radioactive DMDHEU solution. The samples were kept in an upright position for 10 minutes, whereupon the test tube was upended and kept in this position for 15 minutes. The samples were then removed from the test tube and passed through a small laboratory padder for an average wet pickup of 105% (equivalent to a radioactivity of 2.80 microcuries per square centimeter—$\mu Ci/cm^2$) for the all-cotton sheeting and of 100% (equivalent to a radioactivity of 2.67 $\mu Ci/cm^2$) for the 50/50 cotton-polyester sheeting. The equivalent radioactivity per square centimeter was based on the total radioactivity of the solution.

The limited quantity of solutions containing the labeled agents necessitated the use of a somewhat different procedure than was the case with the unlabeled agents, where larger quantities of cross-linker, and hence solution, were available. The same overall effect was believed to have been obtained in each case, except that with the labeled materials the lower roll pressures available on smaller equipment led to slightly higher wet pickup.

Aftertreatments of wet fabrics.—Samples were dried at 60° C for 7 minutes and cured at 160° C for 3 minutes. The radiolabeled samples were rinsed in running de-ionized water for 15 minutes to remove unreacted DMDHEU before machine washing. Each set of samples was then machine-washed and tumble-dried. (See "Laundering, Drying, and Associated Test Procedures.") The samples were sealed individually in plastic bags for future tests. The specific activities of fabrics treated with the radiolabeled DMDHEU that was synthesized by the commercial-type procedure after washing and drying were 0.91 $\mu Ci/cm^2$ for the all-cotton sheeting and 0.82 $\mu Ci/cm^2$ for the 50/50 cotton-polyester sheeting. The specific activity for the all-cotton sheeting treated with the radiolabeled DMDHEU from the laboratory procedure (two-component) was 2.8 $\mu Ci/cm^2$. The unexpectedly low specific activity for the fabrics treated with the radiolabeled DMDHEU that was prepared by the commercial-type procedure (three-component) resulted from use of a batch of ^{14}C-labeled formaldehyde having a formaldehyde content of only 45%–60% of that expected.

Laundering, Drying, and Associated Test Procedures

Fabrics were laundered according to AATCC Test Method 124-1978 (Wash Procedure II) or AATCC Test Method 114-1980 (American Association of Textile Chemists and Colorists 1978d, 1980). In washing, no dummy samples were included, and the pH of the wash solution was adjusted to 7.5 before the addition of detergent and during the rinse cycle. (A study had determined that the average pH of water in the United States is 7.5 (Reinhardt et al. 1981) and that the pH of water in New Orleans is abnormally high.) The principal difference between these two washing methods is that method 124 utilizes a detergent

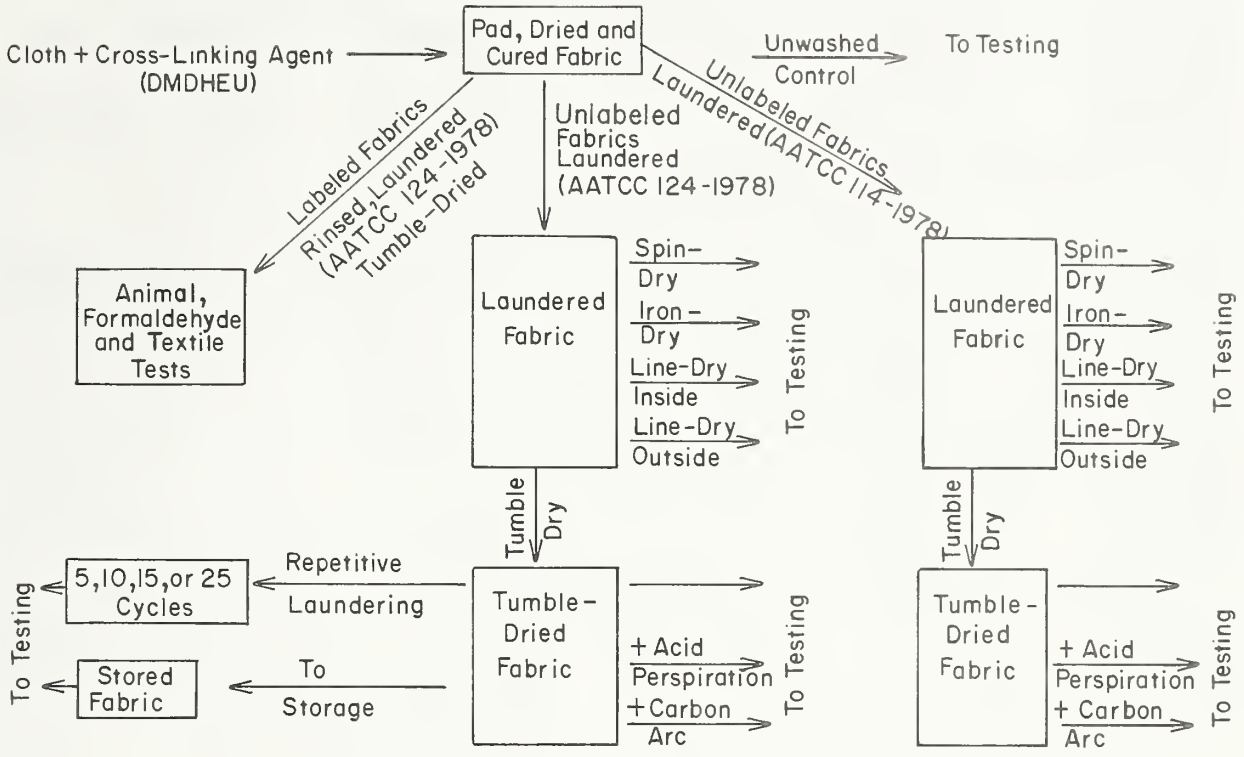


FIGURE 1.—Flow chart showing laundering and drying sequences.

in the washer and method 114 uses a chlorine bleach and a pH of 9.5. The built detergent (method 124) also brings the pH to 9.0–9.5 during the wash procedure. Both procedures have neutral rinses. As such, these two wash procedures provide a contrast of washing with and without bleach. The samples were evaluated after a laundering and:

1. Without drying (after spin-dry cycle on machine).
2. Tumble-drying (AATCC Test Method 123–1978).
3. Iron-drying after spin-dry cycle.
4. Line-drying inside (AATCC Test Method 124–1978).
5. Tumble-drying (AATCC Test Method 124–1978) followed by 16 hours of continuous exposure to carbon-arc light according to AATCC Test Method 16A–1978 (American Association of Textile Chemists and Colorists 1978a).
6. Line-drying outside, by hanging 4 hours in the midday sunlight (in New Orleans).
7. Tumble-drying (AATCC Test Method 124–1978) followed by wetting with synthetic perspiration acid solution according to AATCC Test Method 15–1979 (American Association of Textile Chemists and Colorists 1979) and line-drying the perspiration-wet sample.

The synthetic perspiration solution had a pH of 4.3 and contained 1% sodium chloride and small amounts of lactic acid, disodium hydrogen phosphate, and histidine monohydrochloride.

The carbon-arc test method is an accelerated method by which samples are exposed to a carbon arc for a fixed period of time. The test is generally employed with outdoor fabrics, in which strength before and after exposure is measured, or with colored fabrics, in which change in color is measured. In this instance, formaldehyde release before and after exposure to the carbon arc was measured. The 16-hour period should have been equal to an extended period of continuous exposure to sunlight. The outside line-drying was performed during February, but measurements at SRRC have indicated that in 4 hours in February fabric is exposed to 80% of the sunlight

energy that it would receive if it were line-dried for 4 hours in July. Therefore, the difference in line-drying to time of year was not deemed substantial.

Synthetic perspiration was added to samples (item 7) until they were dripping wet. Wet pickup of perspiration was 53%–63%. Samples in the repetitive washings were also evaluated after zero, 1, 5, 10, 15, and 25 multiple launderings and tumble-dryings done in accordance with AATCC Test Method 124–1978. Adjustment of pH was performed as previously described.

Also, after one laundering and tumble-drying (AATCC Test Method 124–1978), samples were stored (1) by hanging them separately in a metal locker for 1, 2, 3, and 12 months and (2) by wrapping them in plastic bags and placing them in metal foil for 1, 2, 3, and 12 months.

A flow chart (fig. 1) is presented to facilitate understanding of the laundering and drying sequence.

Wrinkle Recovery

Wrinkle recovery of the fabrics was assessed by AATCC Test Method 66–1978 (American Association of Textile Chemists and Colorists 1978b), which measures fabric resiliency. Small samples of fabrics were creased and compressed, and the angle to which the fabric opened was measured—the higher the angle, the more resilient the fabric.

Measuring Formaldehyde

Total formaldehyde content was determined on the distillate from cured, washed samples that were hydrolyzed in a boiling sodium sulfate-sulfuric acid solution by the chromotropic acid method of Roff (1956). Formaldehyde release was determined by AATCC Test Method 112–1978 (sealed-jar method). Free formaldehyde content was determined by the cold sodium sulfite method of DeJong and DeJonge (1952) with 0.5 *N* Na_2SO_3 and 0.01 *N* I_2 solutions. This procedure represented a modification to increase sensitivity by substituting the 0.5 *N* Na_2SO_3 and 0.01 *N* I_2 solutions for the 2 *N* Na_2SO_3 and 0.1 *N* I_2 solution normally used in the test.

DISCUSSION OF FORMALDEHYDE ANALYSES

The lower limits of detection have not been determined for the analysis of total formaldehyde content. If chromotropic acid is the color-development agent, the 0.001 absorbance unit is equivalent to 1×10^{-4} mg of formaldehyde. If only the analytical portion of the test is considered, the cold sodium sulfite method of analysis, as performed in this project, had a detection limit of 7 p/m of formaldehyde based on 1 g of fabric. The deviations about the mean for each sample in this report are representative of that experienced by the authors in other research. In the sealed-jar test (AATCC Test Method 112–1978), the lower limits of detection have not been established. The smallest possible difference in absorbance units is 0.001 unit, which if only the analytical portion of the test is considered, relates to 2 p/m of formaldehyde based on 1 g of sample weight. The deviations about the mean for each sample in this report are representative of those experienced by the authors in other research. Andrews, Reinhardt et al. (1980) presented a statistical analysis of variance of an interlaboratory evaluation of formaldehyde release analyses on fabrics from four finishing treatments. For a DMDHEU treatment, the extremes in means among three laboratories were 161 p/m for unwashed fabrics and 37 p/m for laundered fabrics.

Formaldehyde, then, is measured by three broadly different methods. In the analysis for total formaldehyde, the strong acid hydrolyzes all the finish, and the generated formaldehyde is collected and analyzed. As indicated, all the formaldehyde in the fabric is measured, even that in the most stable of chemical cross-links. In the sealed-jar method (AATCC Test Method 112–1978), a sample of fabric is suspended over water in a sealed Mason jar, the jar is heated at 49° C for 20 hours, and then the water in the jar is analyzed for formaldehyde. This method measures the amount of formaldehyde removed from the fabric under the conditions of temperature and high humidity that are utilized in the test. Research has shown that this procedure causes some hydrolysis of chemical bonds and that the high humidity is a major factor in the amount of formaldehyde generated. The data from this test have become almost a fabric specification in the textile industry, and many fabric buyers rely on this test when setting upper

Table 1.—Analyses of radiolabeled and unlabeled sheetings finished with DMDHEU

Fabric sample	Total HCHO (%)	HCHO release (p/m) by—		Wrinkle recovery angle (degrees)			Level of radioactivity[1] (dis/min/cm²)
		Sealed-jar test	Cold Na_2SO_3	Warp	Filling	Total	
UNLABELED SAMPLES							
3-component system:							
All-cotton	2.38	513	16	131	135	266	
50/50 cotton-polyester	2.01	464	13	139	144	283	
2-component system, all-cotton	2.34	605	15	132	145	277	
RADIOLABELED SAMPLES							
3-component system:							
All-cotton	2.29	237	14	142	135	277	1.997×10^6 (0.90)
50/50 cotton-polyester	1.88	173	11	140	147	287	1.799×10^6 (0.81)
2-component system, all-cotton	2.59	589	11	146	150	296	6.200×10^6 (2.84)
UNTREATED CONTROL SAMPLES							
All-cotton		12	0	100	92	192	
50/50 cotton-polyester		10	0	133	137	270	

[1]Values in parentheses indicate number of $\mu Ci/cm^2$.

limits on formaldehyde release. The cold sodium sulfite method measures the amount of formaldehyde in the fabric available for reaction with sodium sulfite under the conditions of the test, namely a temperature range of 0°–10° C and a pH of 9.5. The fabric itself is directly analyzed in an aqueous medium. This test has been devised to measure the "free" formaldehyde in the fabric, which represents formaldehyde that is absorbed on fabric or that is so loosely bound chemically (hemiacetals) that it is readily available for reaction under very mild conditions to form the bisulfite addition product.

RESULTS AND DISCUSSION

Labeled Fabrics

Analytical data are given in table 1 for fabrics finished with radiolabeled DMDHEU for comparison with data for fabrics finished with unlabeled DMDHEU. The fabrics contained about 2% total bound formaldehyde (by weight), with somewhat lower values for the polyester-cotton fabrics than for the all-cotton fabrics. Based on their total formaldehyde content and wrinkle recovery angles, finished labeled fabrics were deemed to have had satisfactory durable-press treatments. The tendency of the blended fabrics to give a lower wet pickup than the all-cotton fabrics in padding accounts for the lower total formaldehyde content of the blends than of the all-cotton fabrics.

The disparity in the magnitude of the various formaldehyde values are of interest. Thus, while total formaldehyde content was about 20,000 p/m, free formaldehyde, as measured by the cold sodium sulfite method, was only 11–15 p/m. The intermediate values from the sealed-jar test (200–600 p/m) reflect the harsher conditions of this test, which resulted in hydrolysis of certain moieties and thus generation of formaldehyde. (Andrews and Harper 1980).

The complex nature of possible chemical byproducts and the inexact nature of analytical procedures for certain functional groups make it difficult to identify with certainty the chemical source of the formaldehyde generated in the sealed-jar test.

In the reaction with cellulose, DMDHEU has four potentially reactive sites, two of which are pendant *N*-methylol groups, that have the potential to contribute to formaldehyde release. As such, there is the potential for monosubstituted

or disubstituted cellulose, in which a chemical structure is formed with a pendant *N*-methylol group. Such a structure as this, or other byproducts containing formaldehyde or even hydrolysis of the cross-link itself (Andrews and Harper 1980), could be the source of the formaldehyde release value in the sealed-jar test.

Generally, in terms of formaldehyde release, there does not seem to be a clearcut advantage in the use of a two-component system rather than a three-component system for synthesis of DMDHEU. Fabric performance properties, total formaldehyde values, and cold sodium sulfite values are essentially the same for the unlabeled fabrics in table 1. The sealed-jar values (513 vs. 605 p/m) are in the same general level of magnitude. For the labeled fabrics, the sealed-jar values from the three-component system are somewhat lower than anticipated. However, since other values are consistent with a good cross-linking treatment, it was deemed feasible to use these fabrics for animal testing.

The difference in the radioactivity values stems from the fact that separate batches of labeled formaldehyde of marked difference in purity were used for the three-component and two-component systems. The levels of radioactivity of the samples were about 1.8×10^6 and 2.0×10^6 disintegrations per minute per square centimeter (dis/min/cm^2) for the fabrics treated with the three-component reagent and 6.2×10^6 dis/min/cm^2 for the fabrics treated with the two-component reagent.

Unlabeled Fabrics

Unlabeled cross-linked fabrics were prepared to provide samples to evaluate formaldehyde release under conditions that might be encountered during usage by consumers. As previously mentioned, the conditions evaluated included laundering once and drying under various conditions, multiple laundering and tumble-drying, and storing for various periods of time.

Tables 2–7 give data for cotton and 50/50 cotton-polyester fabrics finished with DMDHEU prepared from either two or three components. In general, formaldehyde release values followed the same pattern irrespective of whether DMDHEU was derived from two or three components, whether cotton or blended fabric was used, or whether or not chlorine bleach was used in washing. The overall pattern indicates that washing and drying or aeration resulted in lower formaldehyde release values, whether measured by the cold sodium sulfite method or by the sealed-jar test. Exceptions to these generalizations and the influence of other processing conditions on formaldehyde release are discussed below.

The data in tables 2 and 3 show that substantially lower formaldehyde release values were obtained by the cold sodium sulfite method than by the sealed-jar method. Relatively low values were obtained by the cold sodium sulfite method except in three instances, namely samples taken after spin-drying in a washer, after 16 hours of exposure to a carbon arc, and after five launderings. The values after the carbon-arc treatment are understandable because a 16-hour exposure is estimated to be equal to 2–3 weeks[5] of exposure to sunlight (Yeadon and Harper 1980), and slow breakdown of organics to ultraviolet exposure might be expected. The somewhat higher values from the fabric after the spin-dry cycle in the cold sodium sulfite analysis may reflect the action of washing, the aftereffects of which are not removed until the fabrics are dried. (Repetition of this procedure on analogous samples showed that the values were 35 p/m after spinning and 14 p/m after drying, a somewhat lower differential than that observed in the samples reported in this study.) These results suggest that drying lowers the free formaldehyde content of fabric. The high values for free formaldehyde in the cold sodium sulfite test for the five wash samples were unexpected and are currently inexplicable. Thus, the value for free formaldehyde (cold sodium sulfite method) was 15 p/m after 1 washing and tumble-drying, 98 p/m after 5 washings, and 14 p/m after 10 washings (table 2). There is no reasonable answer for these results, and further investigation is needed to ascertain whether this is a real phenomenon or whether something out of the ordinary happened during the five washings. When the five-wash samples were laundered one additional time, formaldehyde release values averaged 19 p/m in the cold sodium sulfite tests. These data suggest that the very high values after five washings are further suspect. Similar, less drastic trends were noted in the cold sodium sulfite

(*Continued on page 15.*)

[5]This approximation was based upon comparisons between fabrics treated with fire retardant that were tested in a Weather-Ometer and those exposed to the outdoors.

Table 2.—Formaldehyde release from and free formaldehyde content and wrinkle recovery angles of unlabeled 100% cotton sheeting treated with 3-component DMDHEU and laundered without chlorine bleach[1]

Aftertreatment	Free HCHO (p/m), cold Na_2SO_3 method				HCHO release (p/m), sealed-jar method				Wrinkle recovery angle (degrees)								
									Warp				Filling				Total Avg.
	Sample			Avg.	Sample			Avg.	Sample			Avg.	Sample			Avg.	
	A	B	C		A	B	C		A	B	C		A	B	C		
No drying after spin-dry cycle	100	100	99	100	635	633	644	637	119	125	122	122	137	137	136	137	259
Tumble-dry	13	21	14	16	509	525	504	513	130	132	130	131	134	131	141	135	266
Iron-dry after spin cycle	27	27	27	27	419	396	417	411	131	126	134	130	142	153	139	145	275
Line-dry inside	19	20	19	19	439	452	455	449	128	131	127	129	137	139	137	138	267
Tumble-dry, 16 hours, carbon-arc light	54	54	53	54	601	593	652	615	123	121	119	121	135	139	136	137	258
Line-dry outside, 4 hours midday sun	13	13	13	13	460	439	458	452	134	131	132	132	147	141	138	142	274
Tumble-dry, acid perspiration	13	0	14	9	364	343	384	364	131	129	131	130	132	134	145	137	269
Unwashed control	33	46	33	37	941	850	...	895	...	...	...		...	...	...		
5 launderings & tumble-dry	119	51	125	98	317	322	308	316	131	134	132	132	140	137	134	137	269
10 launderings & tumble-dry	14	14	13	14	226	202	245	224	131	129	135	132	138	141	135	138	270
15 launderings & tumble-dry	7	7	7	7	230	266	241	246	120	126	127	124	136	137	130	134	258
25 launderings & tumble-dry	7	7	7	7	168	162	202	177	128	124	127	126	129	135	139	134	260
Tumble-dry, hang in locker 1 month	7	7	7	7	372	356	346	358	130	132	130	131	140	141	142	141	272
Tumble-dry, hang in locker 2 months	15	14	7	12	186	217	194	199	129	127	130	129	138	143	137	139	268
Tumble-dry, hang in locker 3 months	7	7	7	7	179	164	178	174	131	129	131	130	141	142	141	141	271
Tumble-dry, hang in locker 12 months	6	7	7	7	146	131	138	138	134	131	132	132	148	149	148	148	280
Tumble-dry, store in plastic/foil 1 month	13	13	14	13	550	550	550	550	132	133	131	132	140	139	146	142	274
Tumble-dry, store in plastic/foil 2 months	20	14	21	18	457	457	478	464	128	128	135	130	142	140	140	141	271
Tumble-dry, store in plastic/foil 3 months	20	20	20	20	441	438	437	439	136	131	132	134	137	147	144	143	280
Tumble-dry, store in plastic/foil 12 months	19	13	13	15	510	527	537	525	135	134	135	135	149	149	148	149	284

[1]Laundered as specified by AATCC Test Method 124–1978 (Wash Procedure II).

Table 3.—Formaldehyde release from and free formaldehyde content and wrinkle recovery angles of unlabeled 100% cotton sheeting treated with 3-component DMDHEU and laundered with chlorine bleach[1]

Aftertreatment	Free HCHO (p/m), cold Na_2SO_3 method				HCHO release (p/m), sealed-jar method				Wrinkle recovery angle (degrees)								
									Warp				Filling				Total Avg.
	Sample			Avg.	Sample			Avg.	Sample			Avg.	Sample			Avg.	
	A	B	C		A	B	C		A	B	C		A	B	C		
No drying after spin-dry cycle	93	93	93	93	532	549	521	534	129	136	121	128	135	131	132	133	261
Tumble dry	0	7	7	5	500	501	491	497	130	129	127	129	140	145	137	141	270
Iron-dry after spin cycle	7	7	7	7	547	590	550	562	128	131	130	130	136	136	140	137	267
Line-dry inside	0	7	0	2	289	334	328	317	122	123	126	124	137	134	137	136	260
Tumble-dry, 16 hours carbon-arc light	81	79	79	80	811	796	802	803	122	121	127	123	141	144	139	141	264
Line-dry outside, 4 hours midday sun	6	6	6	6	238	231	226	232	132	131	131	131	136	141	137	138	269
Tumble dry, acid perspiration	7	7	6	7	181	177	193	184	126	124	123	124	138	140	134	137	261

[1]Chlorine bleach used according to AATCC Test Method 114-1980. Laundered as specified by AATCC Test Method 124-1978 (Wash Procedure II).

Table 4.—Formaldehyde release from and free formaldehyde content and wrinkle recovery angles of unlabeled 50/50 cotton-polyester sheeting treated with 3-component DMDHEU and laundered without chlorine bleach[1]

Aftertreatment	Free HCHO (p/m), cold Na_2SO_3 method				HCHO release (p/m), sealed-jar method				Wrinkle recovery angle (degrees)								
									Warp				Filling				Total Avg.
	Sample			Avg.	Sample			Avg.	Sample			Avg.	Sample			Avg.	
	A	B	C		A	B	C		A	B	C		A	B	C		
No drying after spin-dry cycle	121	120	121	121	533	556	541	543	135	137	135	136	145	143	139	142	278
Tumble-dry	13	13	13	13	455	471	467	464	140	138	138	139	145	143	144	144	283
Iron-dry after spin cycle	13	13	13	13	384	388	398	390	134	135	137	135	148	146	144	146	281
Line-dry inside	7	7	7	7	...	...	...	...	136	141	136	138	143	142	148	144	282
Tumble-dry, 16 hours carbon-arc light	14	8	7	10	...	...	...	...	137	136	132	135	142	143	139	141	276
Line-dry outside, 4 hours midday sun	7	7	7	7	...	...	...	...	134	140	137	137	142	143	146	144	281
Tumble-dry, acid perspiration	14	8	7	10	...	...	...	...	133	134	136	134	142	140	135	139	273
Unwashed control	13	13	14	13	...	...	...	...	...	...	...	...	...	...	...	...	...
5 launderings & tumble-dry	35	22	43	33	...	...	...	...	137	135	137	136	142	148	141	144	280
10 launderings & tumble-dry	7	7	7	7	...	...	...	...	132	133	135	133	138	139	135	137	270
15 launderings & tumble-dry	7	7	7	7	...	...	...	...	136	132	125	131	137	139	130	135	266
25 launderings & tumble-dry	7	7	7	7	...	...	...	...	130	125	130	128	132	134	131	132	260
Tumble-dry, hang in locker 1 month	7	7	7	7	...	...	...	...	137	135	138	137	141	139	136	139	276
Tumble-dry, hang in locker 2 months	7	7	7	5	...	...	...	...	134	138	136	136	145	143	142	143	279
Tumble-dry, hang in locker 3 months	6	0	0	2	...	...	...	...	130	133	140	134	148	150	141	146	280
Tumble-dry, hang in locker 12 months	6	6	7	6	...	...	...	...	132	140	136	136	136	149	148	148	284
Tumble-dry, store in plastic/foil 1 month	13	13	13	13	...	...	...	...	141	137	132	137	138	140	142	140	277
Tumble-dry, store in plastic/foil 2 months	7	7	14	9	...	...	...	...	134	138	140	137	147	145	145	146	283
Tumble-dry, store in plastic/foil 3 months	6	7	7	7	...	...	...	...	139	138	142	140	137	149	142	143	283
Tumble-dry, store in plastic/foil 12 months	20	19	13	17	...	...	...	...	142	142	142	142	145	149	150	148	290

[1]Laundered as specified by AATCC Test Method 124–1978 (Wash Procedure II).

Table 5.—Formaldehyde release from and free formaldehyde content and wrinkle recovery angles of unlabeled 50/50 cotton-polyester sheeting treated with 3-component DMDHEU and laundered with chlorine bleach[1]

Aftertreatment	Free HCHO (p/m), cold Na_2SO_3 method				HCHO release (p/m), sealed-jar method				Wrinkle recovery angle (degrees)								
									Warp				Filling				Total Avg.
	Sample			Avg.	Sample			Avg.	Sample			Avg.	Sample			Avg.	
	A	B	C		A	B	C		A	B	C		A	B	C		
No drying after spin-dry cycle	109	106	107	107	537	532	525	531	131	139	128	133	136	142	131	136	269
Tumble-dry	7	0	0	2	393	440	439	424	148	140	124	137	155	152	145	151	288
Iron-dry after spin cycle	0	0	7	2	399	430	428	419	129	126	134	130	137	137	140	138	268
Line-dry inside	0	0	0	0	...	...	...	...	128	129	135	131	133	138	143	138	269
Tumble-dry, 16 hours carbon-arc light	39	40	39	39	...	...	...	...	134	132	137	134	141	141	140	141	275
Line-dry outside, 4 hours midday sun	0	0	0	0	...	...	...	...	135	132	134	134	141	146	137	141	275
Tumble dry, acid perspiration	6	6	0	4	...	...	...	...	130	129	131	130	138	140	133	137	267

[1]Chlorine bleach used according to AATCC Test Method 114–1980. Laundered as specified by AATCC Test Method 124–1978 (Wash Procedure II).

Table 6.—Free formaldehyde content and wrinkle recovery angles of unlabeled 100% cotton sheeting treated with 2-component DMDHEU and laundered without chlorine bleach[1]

Aftertreatment	Free HCHO (p/m), cold Na_2SO_3 method				Wrinkle recovery angle (degrees)								
					Warp				Filling				Total Avg.
	Sample			Avg.	Sample			Avg.	Sample			Avg.	
	A	B	C		A	B	C		A	B	C		
No drying after spin-dry cycle	96	95	94	95	130	125	131	129	137	137	136	137	266
Tumble-dry	20	13	13	15	129	131	136	132	143	151	141	145	277
Iron-dry after spin cycle	27	27	27	27	132	135	132	133	135	136	139	137	270
Line-dry inside	7	7	7	7	127	134	126	129	145	147	142	145	274
Tumble-dry, 16 hours carbon-arc light	46	46	40	44	130	128	125	128	135	137	137	136	264
Line-dry outside, 4 hours midday sun	13	13	13	13	130	131	128	130	130	137	131	133	263
Tumble-dry, acid perspiration	7	14	7	9	130	129	124	128	138	143	131	137	265
Unwashed control	20	14	13	16	...	...	...	...	...	...	...	...	...
5 launderings & tumble-dry	43	44	181	89	130	135	131	132	136	143	141	140	272
10 launderings & tumble-dry	7	7	7	7	128	134	131	131	143	140	136	140	271
15 launderings & tumble-dry	7	7	7	7	129	127	129	128	135	132	129	132	260
25 launderings & tumble-dry	7	7	7	7	124	126	127	126	129	128	128	128	254
Tumble dry, hang in locker 1 month	7	7	7	7	136	128	130	131	138	146	143	142	273
Tumble dry, hang in locker 2 months	7	7	14	9	127	130	126	128	137	141	140	139	267
Tumble dry, hang in locker 3 months	7	7	7	7	122	129	132	128	141	141	136	139	267
Tumble dry, hang in locker 12 months	7	7	7	7	135	135	136	135	146	142	146	145	280
Tumble dry, store in plastic/foil 1 month	13	14	14	14	125	131	135	130	132	138	140	137	267
Tumble dry, store in plastic/foil 2 months	7	7	14	9	132	132	127	130	147	147	142	145	275
Tumble dry, store in plastic/foil 3 months	14	13	13	13	134	126	128	129	144	147	141	144	273
Tumble dry, store in plastic/foil 12 months	13	13	13	13	131	134	134	133	144	148	140	144	277

[1]Laundered as specified by AATCC Test method 124–1978 (Wash Procedure II).

Table 7.—Free formaldehyde content and wrinkle recovery angles of unlabeled 100% cotton sheeting treated with 2-component DMDHEU and laundered with chlorine bleach[1]

Aftertreatment	Free HCHO (p/m), cold Na_2SO_3 method				Wrinkle recovery angle (degrees)								
					Warp				Filling				Total Avg.
	Sample			Avg.	Sample			Avg.	Sample			Avg.	
	A	B	C		A	B	C		A	B	C		
No drying after spin-dry cycle	65	66	64	65	130	126	127	128	133	143	137	138	266
Tumble-dry	0	7	0	2	127	130	130	129	145	147	140	144	273
Iron-dry after spin cycle	7	7	7	7	128	129	130	129	146	143	139	143	272
Line-dry inside	7	0	0	2	129	131	128	129	130	131	137	133	262
Tumble-dry, 16 hours carbon-arc light	53	52	53	53	126	129	119	125	136	143	134	138	263
Line-dry outside, 4 hours midday sun	0	7	7	5	125	125	130	127	141	145	132	139	266
Tumble-dry, acid perspiration	7	7	0	5	122	124	129	125	137	136	139	137	262

[1]Chlorine bleach used according to AATCC Test Method 114-1980. Laundered as specified by AATCC Test Method 124-1978 (Wash Procedure II).

values for other fabrics after five washings. Thus, the 50/50 polyester-cotton treated with the three-component DMDHEU gave formaldehyde values in the cold sodium sulfite test of 13 p/m after 1 laundering, 33 p/m after 5 launderings, and 7 p/m after 10 launderings (table 4). A parallel series of values was also observed in the 100% cotton sheeting treated with the two-component DMDHEU (table 6). In all instances, multiple laundering resulted in minimal values in the cold sodium sulfite test.

Two other lesser trends noticeable in the formaldehyde values (cold sodium sulfite test) were the tendency of chlorine-washed samples (AATCC Test Method 114-1980) to show somewhat higher values after carbon-arc exposure (tables 3 and 5) and the tendency of polyester-containing samples, washed with and without chlorine bleach, to show somewhat lower values after carbon-arc exposure than comparable all-cotton samples.

The high values for the samples washed in chlorine and exposed to the carbon arc may have been due to the action of light on N-Cl bonds present, thus leading to more rapid radical-induced breakdown in the system. Similarly, the polyester may have contained antimony oxide or another agent that tended to screen out the effect of light on the fiber, thus decreasing the rate of breakdown in the system. Otherwise, there was not much effect on cold sodium sulfite values from the type of laundry procedure (tumble-drying, tumble-drying and perspiration, line-drying, or iron-drying) for normal fabric or chlorine-bleached fabric, two- or three-component systems, or cotton or blended fabrics.

In the sealed-jar test (table 2), the unwashed cross-linked fabric contained 895 p/m of released formaldehyde and contained 637 p/m after spin-drying and 513 p/m after tumble-drying. Other methods, such as line-drying, iron-drying, or tumble-drying (acid perspiration), gave lower values. Finally, with repetitive launderings, values dropped off to 513 p/m after one washing, 316 p/m after 5 washings, 224 p/m after 10 washings, 246 p/m after 15 washings, and 177 p/m after 25 washings. These data suggest that the long-term values for formaldehyde release with this system from the sealed-jar test average about 200 p/m. Because the values for formaldehyde release in the cold sodium sulfite test after 15 and 25 launderings are relatively minute, we conclude that the combination of heat and moisture caused this level of breakdown in finish. According to data from the cold sodium sulfite analysis there is no anomaly after five washes.

The increased values from the cold sodium sulfite test for fabrics after carbon-arc exposures were also mirrored in increased sealed-jar values. As previously stated, carbon-arc exposure of 16 hours approximates 2-3 weeks of exposure to sunlight (Yeadon and Harper 1980). Thus, it is expected that little, if any, effect on formaldehyde release occurred in samples that were line-dried for 4 hours.

The other phase of this work was that related to storage. While cold sodium sulfite values are minuscule for fabric stored wrapped or unwrapped for 1, 2, 3, and 12 months, there was a progressive decrease in formaldehyde release values (sealed-jar test) for fabric stored unwrapped in a locker. Thus, sealed-jar values (table 2) decreased from 513 p/m initially to 358 p/m after 1 month, to 199 p/m after 2 months, to 174 p/m after 3 months, and to 138 p/m after 12 months. Again, these data suggest that a plateau of about 150-200 p/m is reached in the sealed-jar test with this particular finish. These collective data also suggest that formaldehyde release from such fabrics can be lowered by either laundering or aeration. In actual practice, a combination of the two methods probably leads to rapid attainment of very low values for the cold sodium sulfite test and relatively low values for the sealed-jar test.

By contrast, the samples that were wrapped in plastic and foil showed very little change with storage, which reflects that formaldehyde was free to escape from the locker samples but not from the plastic-wrapped samples.

Many current unwashed commercial fabrics exhibit formaldehyde release values of 300-500 p/m in the sealed-jar test (Pai and Petersen 1981, Wayland et al. 1981), which is substantially less than the 895 p/m for the unwashed cross-linked cotton fabric used in this research. The lower levels of formaldehyde release arise from the use of lower levels of cross-linking agent than reported here, improved agents, presence of additives, and probably the use of large-scale equipment. Certainly, it should be realized that in blended fabrics essentially all of the cross-linking agent goes to the cotton component (Harper and Bruno 1972), and therefore, lower levels of agent treatment are sufficient to achieve a given level of cross-linking in the cotton component.

SUMMARY

A series of ^{14}C-labeled durable-press cotton fabrics and cotton-polyester fabrics was prepared to determine the influence of various combinations of laundering and storing procedures on formaldehyde release. The finishing agent used in this study was dimethyloldihydroxyethyleneurea (DMDHEU) prepared by either two- or three-component synthesis. The DMDHEU was prepared from ^{14}C-labeled formaldehyde for future transfer experiments to determine whether any of the labeled formaldehyde would pass through animal skin.

Laundering and storing experiments were also performed with unlabeled durable-press fabrics from treatments with similarly synthesized cross-linking agents.

In general, the laundering and storage tests showed declining values of formaldehyde release with laundering or storage, whether measured by the cold sodium sulfite method or the sealed-jar method. However, there were exceptions in the values for the cold sodium sulfite method after the spin-dry cycle of the wash (before drying), after exposure to a carbon arc, and after laundering five times. The latter instance was unexpected and needs further verification. By contrast, sealed-jar values decreased in almost every instance, when compared with original sample values, during laundering or storing of samples. Somewhat surprising was the magnitude of the loss of formaldehyde in storage, as revealed by sealed-jar test values after 1, 2, 3, and 12 months.

There was generally little effect on formaldehyde release, whether the DMDHEU was prepared from a two- or three-component system. No evaluation was made on the influence of chemical modifications (use of methylated agents, glycols, or the more stable carbamate finishes) utilized in industry to produce fabrics with lower initial levels of formaldehyde release than those employed in this study.

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